different rates with acetylenedicarboxylic acid, the monoanion of acetylenedicarboxylic acid and the dianion of acetylenedicarboxylic acid. They have also detected a $\mathrm{Cr^{II}}$ complex, of unknown geometry, with acetylenedicarboxylic acid.

We have observed, however, that the dianion of acetylenedicarboxylic acid gave no evidence of reaction with $[\mathrm{Co(CN)_5}]^{3-}$ at pH 13.30. A reaction did occur, as evidenced by a color change, when the pH was lowered to 10–11.[18]

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[18] Preliminary kinetic studies of $[\mathrm{Co(CN)_5}]^{3-}$ and $\mathrm{CH_3CO_2C{\equiv}CCO_2CH_3}$ show the kinetics to be complicated. The reaction rate is drastically reduced when the alkoxy carbon chain is increased.

Contribution from the Department of Chemistry,
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A New Method for the Preparation of Fluorodisulfate Salts

By Darryl D. Des Marteau and George H. Cady

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The only reported fluorodisulfate salt is that of potassium. It was prepared by the reaction of potassium fluoride with excess sulfur trioxide.[1]

$$\mathrm{KF + 2SO_3 = KS_2O_6F = KSO_3F + SO_3}$$

The white crystalline compound was unstable and decomposed completely to potassium fluorosulfate and sulfur trioxide when heated to 100° for 4 hr. Calcium fluorodisulfate has been suggested as an intermediate in the reaction of calcium fluoride with sulfur trioxide.[2]

Potassium, sodium, and, probably, ammonium fluorodisulfates have now been produced by reaction of peroxydisulfuryl difluoride with the corresponding peroxydisulfates, the potassium and sodium salts being

$$\mathrm{M_2[O_3SOOSO_3] + FO_2SOOSO_2F = 2M[O_3SOSO_2F] + O_2}$$

$$\mathrm{2M[O_3SOSO_2F] = 2M[SO_3F] + 2SO_3 \quad (M = K, Na, or NH_4)}$$

obtained in high yield. The ammonium salt was impure and was obtained in approximately 15% yield.

Experimental Section

Reagents.—Peroxydisulfates of sodium, potassium, and ammonium were obtained from commercial sources and were dried by warming *in vacuo*. Peroxydisulfuryl difluoride ($\mathrm{S_2O_6F_2}$) was prepared by the reaction of fluorine with sulfur trioxide using a procedure similar to that of Shreeve and Cady.[3] [Since a by-product of this process, $\mathrm{SO_3F_2}$ (bp −31.3°), is now known to probably be explosive, it is advisable to collect only that part of the product which condenses in a trap at −78°. Most of the gaseous $\mathrm{SO_3F_2}$ is carried through the trap by a stream of nitrogen used in the process and discarded in a fume hood. Peroxydisulfuryl difluoride alone is not explosive, but it can form explosive mixtures with various reducing agents.]

Preparation and Analysis.—The reactions were carried out in a Pyrex-glass bulb fitted with a Fischer-Porter glass valve closed by a Teflon stem. $\mathrm{S_2O_6F_2}$ was condensed onto the dried, powdered peroxydisulfate at −183° and the mixture was then allowed to warm to room temperature. A slow reaction took place near room temperature liberating oxygen. An approximate 10:1 mole ratio of $\mathrm{S_2O_6F_2}$ to $\mathrm{M_2S_2O_8}$ was used in each case. The reactions were very slow and became slower with time, probably owing to surface effects. Oxygen was removed periodically by pumping on the reaction vessel at −183°. After no further oxygen was observed to form [21 days for 1.7384 g of $\mathrm{K_2S_2O_8}$, 4 days for 1.0339 g of $\mathrm{Na_2S_2O_8}$, 8 days for 1.0356 g of $\mathrm{(NH_4)\text{-}S_2O_8}$], the excess $\mathrm{S_2O_6F_2}$ was removed by pumping at room temperature until the rate of weight loss was only a few milligrams per hour. The products could not be pumped to constant weight because the unstable fluorodisulfate salts dissociated slowly into $\mathrm{SO_3}$ and $\mathrm{MOSO_2F}$ at room temperature. For the above samples of $\mathrm{K_2S_2O_8}$ and $\mathrm{Na_2S_2O_8}$ the weights of product were 2.743 and 1.718 g, respectively (theory: 2.807 and 1.756 g). For the sample of $\mathrm{(NH_4)_2S_2O_8}$ the weight of product was 1.169 g (1.789 g, theory) and corresponded to approximately 15% $\mathrm{NH_4S_2O_6F}$ mixed with 85% $\mathrm{NH_4SO_3F}$. The products were then heated to 135° maximum and pumped to constant weight. After this treatment the above samples weighed 1.760, 1.073, and 1.035 g, respectively, corresponding closely to the theoretical weights 1.770, 1.060, and 1.063 g, respectively, for $\mathrm{KSO_3F}$, $\mathrm{NaSO_3F}$, and $\mathrm{NH_4SO_3F}$. Other runs were similar to those just described. $\mathrm{KOSO_2F}$, $\mathrm{NaOSO_2F}$, and $\mathrm{NH_4OSO_2F}$ were then hydrolyzed in 1 *N* sodium hydroxide for 10 hr at 100° and the resulting solutions were analyzed for sulfur and fluorine. Sulfur was determined gravimetrically as barium sulfate and fluorine volumetrically by the method of Willard and Winter.[4] The sulfur trioxide was identified qualitatively by its physical properties, by tendency to liberate iodine from aqueous potassium iodide, and by giving a positive test for sulfate after hydrolysis. Oxygen was identified by its mass spectrum and volatility at −183°. The infrared spectrum of the excess peroxydisulfuryl difluoride remaining after reaction corresponded to $\mathrm{S_2O_6F_2}$ containing a trace of $\mathrm{SiF_4}$. Analytical data for the runs given above are summarized in Table I.

Table I

Analytical Data

	Cation		
	$\mathrm{Na^+}$	$\mathrm{K^+}$	$\mathrm{NH_4^+}$
Moles of $\mathrm{O_2}$[a]	0.98	0.99	1.02
Moles of $\mathrm{SO_3}$[b]	0.99	1.00	1.01
F[c] found, wt %	16.2	13.6	16.0
F calcd, wt %	15.6	13.8	16.2
S[c] found, wt %	26.2	22.5	27.6
S calcd, wt %	26.3	23.2	27.3

[a] Per mole of $\mathrm{M_2S_2O_8}$ consumed. [b] Per mole of $\mathrm{MS_2O_6F}$ decomposed by heating. [c] Analysis of $\mathrm{MOSO_2F}$.

X-Ray powder photographs were taken for samples of $\mathrm{KOSO_2F}$ and $\mathrm{KS_2O_6F}$ prepared by the method given above and by the method of Lehmann and Kolditz.[1] The two methods gave materials having essentially the same patterns. These are given in the Ph.D. thesis of the junior author.[5] When the patterns were compared with those reported by Lehmann and Kolditz,[1] the extent of agreement was incomplete. Professor Kolditz has also com-

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pared the data and powder patterns (private correspondence) and agrees with us that the materials obtained by the two methods must be the same even though the reported powder patterns are not exactly the same.

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CONTRIBUTION FROM HYNES CHEMICAL
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The Fluorination of Cyanogen Chloride[1]

BY JOHN B. HYNES, BRIAN C. BISHOP, AND LUCIUS A. BIGELOW

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This report describes the results of a study of the direct and indirect fluorination, employing elemental fluorine or AgF_2, respectively, of the relatively reactive chlorinated nitrile, cyanogen chloride, which is also the most simply chlorinated nitrile. It was shown earlier that the direct fluorination of a number of halonitriles[2] yielded both saturated and unsaturated products containing chlorine and also that direct fluorination of the closely related HCN[3] produced not only CF_3NF_3 in good yield, but also $CF_3N{=}NCF_3$, $(CF_3)_2NF$, and $(CF_3)_3N$. The indirect fluorination of ClCN has been the subject of a number of earlier investigations. In each case the nature of the products formed was markedly dependent upon the experimental conditions and the fluorinating agent employed. For example, when ClCN was passed over AgF_2 at near ambient temperature, $CF_3N{=}NCF_3$ was produced in high yield together with some CF_3NO.[4] However, the analogous reaction with HgF_2 at 290–300° produced $CF_3N{=}CF_2$ and $[(CF_3)_2N]_2Hg$, while CuF_2 at 450° gave cyanuric fluoride,[5] but in none of these cases were any organic compounds isolated which contained chlorine. The autoclave reaction of ClCN with AgF in the presence of chlorine yielded a number of products including CF_3Cl and $CF_3N{=}NCF_3$, together with a small amount of a compound partially characterized as CF_3NCl_2.[6]

It was felt that a further study of both the direct and indirect fluorination of cyanogen chloride might lead to the formation of new and interesting fluorinated derivatives of this compound which also contain chlorine. Accordingly, the direct fluorination of cyanogen chloride was undertaken under mild operating conditions in the jet reactor; *cf.* the Experimental Section. The crude product was separated into portions by rectification, and these were then resolved into their components by gas chromatography. The new compounds produced were the saturated adduct, $CClF_2NF_2$, isolated only in small amount, its isomer, CF_3NClF, bp −32.8°, and the azo compound, $CClF_2N{=}NCF_3$, bp 5.8°.[7] They were accompanied by the expected cleavage products, CF_4, $CClF_3$, CCl_2F_2 and $CF_3N{=}NCF_3$, as well as some free chlorine. It is worthy of note that this appears to be the first time that an organic compound of the general formula RNClF has been reported. Apparently, some chlorine is always displaced from the ClCN giving rise to the nitrene, CF_3N:. This in turn could add ClF, or its component elements, to produce the unexpected compound CF_3NClF.

A comparison of the more significant ions from the mass cracking patterns of the isomers $CClF_2NF_2$ and CF_3NClF appears in Table I. The chlorine isotope ratios were consistent with the ion assignments but the Cl^{37+} ions have been omitted for the sake of brevity.

TABLE I
COMPARATIVE MASS CRACKING PATTERNS OF THE ISOMERS $CClF_2NF_2$ AND CF_3NClF

		Relative Intensities	
m/e	Probable ion	$CClF_2NF_2$	CF_3NClF
31	CF^+	15.0	4.2
33	FN^+	2.8	0.3
35	Cl^+	9.9	3.0
47	CCl^+	1.0	...
49	ClN^+	2.0	35.4
50	CF_2^+	13.6	3.5
52	F_2N^+	1.1	...
64	CF_2N^+	4.9	2.0
66	$CClF^+$	1.6	...
69	CF_3^+	100.0	100.0
83	CF_3N^+	9.1	1.0
85	$CClF_2^+$	44.3	...
99	$CClF_2N^+$	2.6	2.3
102	CF_4N^+	37.7	...
137	$CClF_4N^+$	...	1.6

As seen, these structures are clearly differentiated by the presence or absence of particular ions such as CCl^+, F_2N^+, $CClF^+$, $CClF_2^+$, and CF_4N^+. The formation of the CF_4N^+ ion from $CClF_2NF_2$ in relatively high intensity shows that the loss of chlorine constitutes a primary ionization step for this molecule. The chlorine in CF_3NClF is more difficultly removed as evidenced by the large intensity of the ClN^+ ion and a parent ion which was not exhibited by its isomer. As is true for almost all highly fluorinated organic compounds, the CF_3^+ ion is the most abundant fragment for each compound.

The fluorination of nitriles with AgF_2 in a closed system has been shown to involve nitrene intermediates which dimerize to form azo compounds as prin-

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[1] This material was presented to the Fluorine Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964. This work was supported by the Advanced Research Projects Agency through the Army Research Office (Durham), to whom grateful acknowledgment is hereby made.

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[6] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 2337 (1962).

[7] The compound $CClF_2N{=}NCF_3$ was recently described by V. A. Ginsburgh, A. Ya. Yakubovich, A. S. Filatove, V. A. Shpanskii, E. S. Vlasova, G. E. Zelenin, L. F. Sergienko, L. L. Marlynova, and S. P. Makarov, *Dokl. Akad. Nauk SSR*, **142**, 88 (1962). These workers reported an observed boiling point of 4.5°.